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VERIFICATION OF A TRANSLATION

I, Charles Edward SITCH BA,

Deputy Managing Director of RWS Group Ltd UK Translation Division, of Europa House,
Marsham Way, Gerrards Cross, Buckinghamshire, England declare:

That the translator responsible for the attached translation is knowledgeable in the German language in which the below identified international application was filed, and that, to the best of RWS Group Ltd knowledge and belief, the English translation of the amended sheets of the international application No. PCT/EP2004/051514 is a true and complete translation of the amended sheets of the above identified international application as filed.

I hereby declare that all the statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application issued thereon.

Date: January 27, 2006

Signature :



For and on behalf of RWS Group Ltd

Post Office Address :

Europa House, Marsham Way,
Gerrards Cross, Buckinghamshire,
England.

5 For binding to the substrate surface, the coatings disclosed in DE 101 58 433 A1 need physico-chemical activation thereof, e.g. via corona discharge. Furthermore, for thermally labile substrates, rapid setting of the layers at very low temperatures is essential. For example, in the coating of window profiles composed of PVC, temperatures above 100°C lead to deformation which, however, makes accurate fit impossible during further processing of the profile. The reaction conditions disclosed here have only restricted application to accurately dimensioned products.

Object

20 It was therefore an object of the present invention to provide photocatalytically active coatings which are suitable even for thermally labile or easily oxidized backing materials.

25 Brief description of the invention

The present invention provides a photocatalytically active coating of a substrate composed of at least two layers produced by solution chemistry and with at least one first underlayer applied to the substrate and composed of an inorganic polymer, and comprising the metal oxides SiO₂ and ZrO₂ covalently bonded to one another, and at least one second overlayer composed of TiO₂ particles, where the underlayer comprises less than 0.5% by weight of TiO₂ particles, is pore-free, and comprises SiO₂ and ZrO₂ in a ratio by weight of from 50:50 to 95:5.

The inventive underlayer comprises no pores, completely covers the substrate, and thus provides protection of easily oxidized surfaces from photocatalytically initiated decomposition via the overlayer. This is particularly advantageous in the coating of window profiles composed of PVC, because these likewise comprise titanium dioxide. If the titanium dioxide present in the PCV composition were to be released, the result is a further increase in the decomposition rate of the plastic. The thermal hardening of the underlayer can take place at temperatures sufficiently low to prevent any deformation of molded semifinished products, such as profiles.

Furthermore, the underlayer is substantially free from TiO_2 particles. This means that, starting from the substrate, at least 85%, preferably at least 90%, very preferably at least 95%, of the thickness of the underlayer is practically free from TiO_2 particles, i.e. comprise less than 0.5% by weight and in particular less than 0.1% by weight of TiO_2 particles.

The underlayer can be composed of at least two layers applied in succession of identical or different constitution. The provisos for the content of TiO_2 and ZrO_2 apply to the entirety of the sublayers, but can also be formulated for each individual layer. For example, it is possible for one of the layers to be composed entirely of ZrO_2 and for another layer to be composed of a $\text{SiO}_2/\text{ZrO}_2$ mixture. The sublayers can also have identical constitution but different thickness, e.g. via application of suspensions of different solids content.

Inventive coatings are therefore particularly suitable for the coating of substrates composed of one or more polymeric materials and/or metals. The polymeric

material used can comprise one or more polymers selected from the group of polyvinyl chloride (PVC), polypropylene (PP), polyethylene (PE), polyacrylates and -methacrylates, e.g. polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), polyester, epoxy materials, polyurethanes (PU), polyisocyanates, SBR, ABS, ASA, NBR, or copolymers composed of acrylonitrile, styrene, butadiene, methacrylate, or isoprene, in each case in the form of homo- or copolymer, in the form of coextrudate, or in the form of polymer blend.

The substrates may have been previously molded to give semifinished products, if appropriate with complex geometric shapes, e.g. extruded profiles. Clearly, coextrudates can be used here. For example, semifinished PVC products, such as window profiles or door profiles, can be provided with an outer layer composed of the polymers mentioned, in particular PMMA.

Figure 1 is a diagram of the structure of an inventive coating, S being substrate, U being chemically inert underlayer composed of the inorganic polymer, and P being the photocatalytically active layer composed of TiO_2 particles.

The thickness of the first layer (U in fig. 1, underlayer) in the dry, crosslinked state is preferably from 100 to 500 nm, particularly preferably 200 to 500 nm, and in particular from 300 to 500 nm.

The thickness of the second, photocatalytically active layer (P in fig. 2, overlayer) in the dry state is preferably from 20 to 100 nm, particularly preferably from 20 to 50 nm.

The inorganic polymer of the underlayer(s) is preferably

composed of SiO_2 and of ZrO_2 , optionally with one or more metal oxides covalently bonded to one another from the group of Al_2O_3 , Nb_2O_3 , Ta_2O_3 , CaO . For the purposes of this invention, a compound which is formally composed of the metal oxides mentioned, prepared, for example, by the sol-gel process of DE 101 58 433 A1, is regarded as an inorganic polymer. This also includes the linkage of relatively large units or blocks, e.g. ZrO_2 particles by way of SiO_2 bridges.

Inorganic polymers which comprise SiO_2 and ZrO_2 in a ratio by weight of from 50:50 to 95:5, in particular from 75:25 to 90:10 or from 85:15 to 90:10, have proven successful as underlayer. Layers of this type can optionally also comprise from 0.01 to 2% by weight (based on the underlayer) of at least one other metal oxide, such as Al_2O_3 , Nb_2O_3 , Ta_2O_3 , or CaO , or else carbon in the form of carbon black.

The diameter of the TiO_2 particles of the photocatalytically active overlayer is preferably from 5 to 30 nm, in particular from 10 to 25 nm; it is advisable to use particles of the anatase crystalline form rather than those of rutile structure.

The photocatalytic activity of the TiO_2 particles may have been reduced via the coating process. In order to reactivate the overlayer, the substrates can be exposed to sunlight or to appropriate artificial UV irradiation for from 1 to 5 hours.

The present invention also provides a process for production of photocatalytically active coatings on a substrate via the following steps of the process

- coating of a substrate with an inorganic polymer by solution chemistry via application of a suspension of the inorganic polymer or its chemical precursors in an organic suspension medium,

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b. complete or partial removal of the organic suspension medium, to give an underlayer.

c. application of a dispersion composed of TiO_2 particles in an organic dispersion medium to the
5 underlayer.

d. complete or partial removal of the organic dispersion medium to give an overlayer.

e. heat-treatment of the under- and overlayer at from 20 to 120°C for from 10 to 300 sec,

10 with the proviso that the underlayer is composed of an inorganic polymer, comprises less than 0.5% by weight of TiO_2 particles, is pore-free, and comprises SiO_2 and ZrO_2 in a ratio by weight of from 50:50 to 95:5.

15 Step a of the process

The suspension used in step a) of the process comprises the inorganic polymer or its chemical precursors. Chemical precursors are compounds from which the
20 inorganic polymers or the metal oxides mentioned can be prepared, in particular one or more metal oxides from the group of SiO_2 , ZrO_2 , Al_2O_3 , Nb_2O_3 , Ta_2O_3 , CaO , and/or the corresponding alkoxides, chlorides, nitrates, hydroxides, formates, or acetates, in each case
25 individually or in the form of a mixture.

Particularly suitable starting materials for SiO_2 are silica sol, silica gel, and/or silicic acid, organo-silanes, such as alkoxy- or alkoxyhydroxysilanes, and
30 in particular tetraalkoxysilanes; and for ZrO_2 : the zirconium alkoxides, e.g. zirconium butanolate or zirconium propanolate. The use of other metal oxides, e.g. Al_2O_3 , if appropriate in the form of aluminum-oxide-doped SiO_2 , is optional.

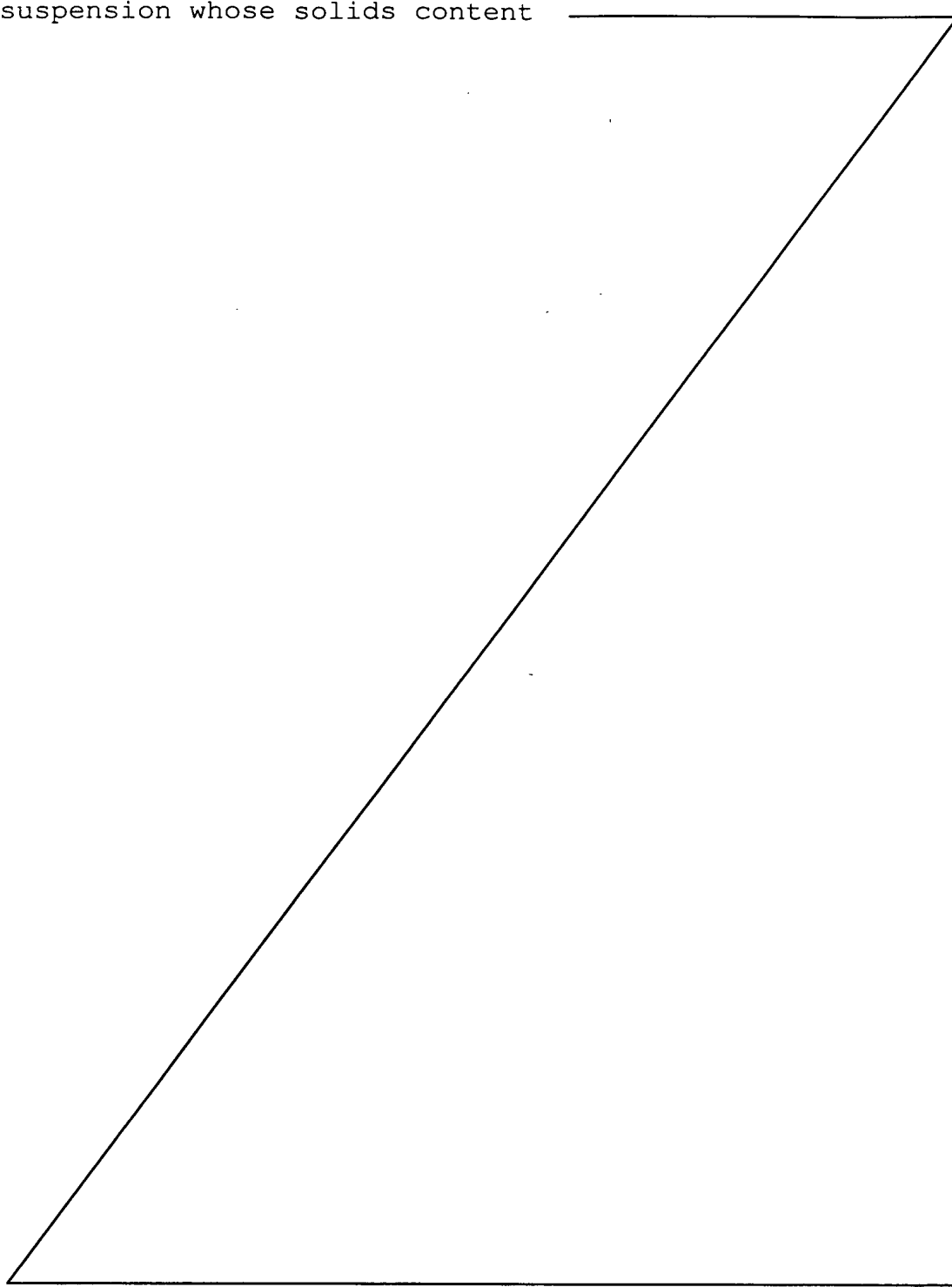
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The solids content of the suspensions in step a) of the process can be from 0.1 to 25% by weight, preferred

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solids contents for obtaining a homogeneous layer here being from 1 to 5% by weight.

One particular variant of the invention uses a
5 suspension whose solids content



What is claimed is

1. A photocatalytically active coating of a substrate
composed of at least two layers produced by
5 solution chemistry and with at least one first
underlayer applied to the substrate and composed
of an inorganic polymer, and comprising the metal
oxides SiO_2 and ZrO_2 covalently bonded to one
another, and at least one second overlayer
10 composed of TiO_2 particles, **characterized in that**
the underlayer comprises less than 0.5% by weight
of TiO_2 particles, is pore-free, and comprises SiO_2
and ZrO_2 in a ratio by weight of from 50:50 to
95:5.
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2. The photocatalytically active coating as claimed
in claim 1, **characterized in that** the inorganic
polymer is composed of one or more metal oxides
covalently bonded to one another from the group of
20 SiO_2 , ZrO_2 , Al_2O_3 , Nb_2O_3 , Ta_2O_3 , CaO .
3. The photocatalytically active coating as claimed
in claim 1 or 2, **characterized in that** the
underlayer is composed of at least two layers
25 applied in succession of identical or different
constitution.
4. The photocatalytically active coating as claimed
in any of claims 1 to 3, **characterized in that** the
30 substrate used comprises one or more polymers
selected from the group of PVC, PP, PE, PMMA, PS,
PC, polyesters, epoxy materials, polyurethanes,
polyisocyanates, SBR, ABS, ASA, NBR, or copolymers
composed of acrylonitrile, styrene, butadiene,
35 methacrylate, or isoprene, in each case in the
form of homo- or copolymer, in the form of
coextrudate, or in the form of polymer blend.

5. A process for production of photocatalytically active coatings on a substrate, characterized by the following steps of the process:
- a. coating of a substrate with an inorganic polymer by solution chemistry via application of a suspension of the inorganic polymer or its chemical precursors in an organic suspension medium,
 - b. complete or partial removal of the organic suspension medium, to give an underlayer.
 - c. application of a dispersion composed of TiO_2 particles in an organic dispersion medium to the underlayer.
 - d. complete or partial removal of the organic dispersion medium to give an overlayer.
 - e. heat-treatment of the under- and overlayer at from 20 to 120°C for from 10 to 300 sec, with the proviso that the underlayer is composed of an inorganic polymer, comprises less than 0.5% of TiO_2 particles, is pore-free, and comprises SiO_2 and ZrO_2 in a ratio by weight of from 50:50 to 95:5.
6. The process as claimed in claim 5, **characterized in that** the suspension used in step a) of the process comprises the metal oxides SiO_2 and ZrO_2 , and also optionally Al_2O_3 , Nb_2O_3 , Ta_2O_3 , CaO , and/or the corresponding alkoxides, chlorides, nitrates, hydroxides, formates, or acetates.
7. The process as claimed in claim 5 or 6, **characterized in that** the organic suspension and dispersion medium comprises ethanol, propanol, isopropanol, isobutanol, n-butanol, glycol, ethylene glycol, propylene glycol, butylene glycol, water, formic acid, and/or acetic acid, alone or in the form of a mixture.

8. The process as claimed in claim 6 or 7,
characterized in that steps a) and b) of the
process are carried out at least twice in
succession.
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9. The process, as claimed in any of claims 6 to 8,
characterized in that steps c) and d) of the
process are carried out at least twice in
succession.
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10. A window profile, a door profile, a roller-shutter
segment, a window sill, an architectural panel, a
door leaf, a gutter, a downpipe, or a plastics or
aluminum shell for the covering of window or door
frames, with a coating as claimed in any of claims
15 1 to 4.